cw laser annealing of Nb_3Al and Nb_3Si

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cw laser annealing has been applied to synthesize the metastable A15 superconductors, Nb_3Al and Nb_3Si. Qualitative agreement with the equilibrium phase diagrams have been obtained for the Nb-Al system. Laser annealing permits the high-temperature A15 phase to be fast quenched to room temperature without decomposition. Subsequent use of multiple low-temperature laser scans raises the superconducting transition temperature, probably by improving the atomic order. For the Nb-Si system, a single-phase nonstoichiometric A15 structure is formed from the amorphous phase upon laser annealing.

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I. INTRODUCTION

The synthesis of metastable superconducting compounds with the A15 crystal structure, such as Nb_3Ge, Nb_3Al, and Nb_3Si, has received considerable attention because of the well-known potential of these materials for high-temperature superconductivity ($T_c > 20$ K). The difficulties that have been encountered in the synthesis are well illustrated by Nb_3Al, which is the least unstable member of the group.[1] Nb_3Al is known to exist as a niobium-rich A15 compound over a large temperature range in the equilibrium phase diagram.[2–4] However, the A15 phase is believed to approach stoichiometry only at relatively high temperatures (1700–1940 °C).[2–4] Hence, even though the exact details of the phase diagram at high temperatures remain unsettled, it is to be expected that a nearly stoichiometric A15 phase will disproportionate at low temperatures unless it is cooled very rapidly. Rapid cooling, on the other hand, tends to freeze in atomic disorder and structural defects. Much of the effort in the synthesis of a high-T_c Nb_3Al has therefore been directed toward finding a suitable compromise between stoichiometry and ordering.

Even greater difficulty is encountered in the synthesis of Nb_3Si, since a stoichiometric A15 phase apparently does not even exist in the equilibrium phase diagram.[5] As a result, materials synthesis procedures that are known to be capable of forming metastable phases are very likely essential to the synthesis of a high-T_c form of Nb_3Si.[6]

Very recently, the deposition of concentrated energy with laser or electron beams has been successfully applied to the modification of electronic materials, including the formation of metastable alloys.[7,8] In particular, a scanning cw laser system, employed for reacting thin metal layers with a single-crystal silicon substrate, has led to several interesting results. In Refs. 7–9, it is shown that both scanning cw laser and electron beam systems can be used to form large-area, uniform, essentially single-phase metal-silicon compounds (silicides). Furthermore, metastable silicides, which have so far proven difficult or impossible to form by either conventional furnace annealing or pulsed-beam annealing, can readily be obtained with cw-beam annealing. In effect, the annealing process using a scanning cw beam can be described as a "high-temperature, short-time furnace." With such a process, the annealing temperature can easily be raised to above 2000 °C by a proper choice of the laser power; the annealing time can be increased by employing multiple laser scans; and heating and cooling rates can be controlled by changing the beam scan speed (up to a maximum cooling rate $\sim 10^6$ °C/sec).

These features are quite attractive for the synthesis of Nb-Al and Nb-Si A15 compounds. For example, it is reasonable to expect that with cw-beam annealing, nearly stoichiometric Nb_3Al can be quenched from a high-temperature A15 state to room temperature without decomposition into low-temperature phases. In addition, the formation of the metastable A15 Nb_3Si phase might be favored by this process. The purpose of this paper is to describe our first attempts to apply cw laser annealing to the synthesis of Nb_3Al and Nb_3Si, and to discuss the preliminary results and the potential application of cw-beam annealing for forming metastable phases of these materials.

II. EXPERIMENTAL

A. Sample preparation

Thin films of Nb-Al (5000 Å) and Nb-Si (1000 Å) were prepared by the electron-beam coevaporation method in a background pressure of $(1.0–3.0)\times 10^{-7}$ Torr. These films were deposited onto a single-crystal Si substrate coated with a thin layer of Si_3N_4 or SiO_2 as a buffer. This substrate is used because (a) single-crystal silicon is a good heat conductor at high temperatures and (b) analytical calculations for the laser-induced temperature rise[12] are well established for a silicon substrate. Typical deposition conditions are as follows: $\sim$30-Å/sec deposition rate and 300 °C substrate temperature for the Nb_3Al, and $\sim$50-Å/sec deposition rate and 500 °C substrate temperature for the Nb_3Si. Further details on the thin-film deposition are given in Refs. 1, 6, and 10.

B. Laser annealing system

The laser used for the annealing was a cw Ar laser operating in the multiline mode. The laser beam was focused by a

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135-mm lens onto the sample surface and was scanned across the sample. The beam spot size after focusing was about 50 μm. Details on the scanning apparatus are described in Ref. 11. The sample was vacuum-chucked to a brass holder, which was heated to 250 ± 1 °C. Laser annealing was performed in an inert ambient (flowing N_2 or Ar).

C. Laser annealing temperature

Laser-beam irradiation produces a Gaussian-like temperature distribution. The peak temperature in the center of the beam is given by[12]

$$T_{\max} = T_k + (T_0 - T_k)\exp[(1-R)P/(\pi)^{1/2}wA], \quad (1)$$

where T_0 is the substrate temperature and T_k and A are constants in the empirical expression for the temperature-dependent thermal conductivity. w is the beam radius, P is the laser output power, and R is the reflectivity of the sample. To determine the laser output power required to achieve a specific temperature, it is necessary to know R and w. R is experimentally measured before each scan and w is determined from Eq. (1) by measuring the power at which the surface of a clean silicon wafer starts to melt ($T_{\max} = 1412$ °C at this power). Since the depth distribution of temperature is constant within a few microns from the surface, the entire thickness of the metal film (0.1–0.5 μm) is heated to a uniform temperature during laser annealing. The error in calculating $T_{\max}$ that arises by using the Si melting power P_{melt} and reflectivity R of the sample is estimated to be $\pm 10\%$ for silicon. Use of this calculated temperature to predict growth rates of metal silicides[13] and impurity diffusion in silicon[14] provides very satisfactory agreement with theory[12] for these applications. However, complications can occur when the sample reflectivity changes during the laser annealing. The uncertainty of the annealing temperature in the present experiments can therefore be substantially larger than the estimate given above.

D. Characterization of films

Laser-annealed samples were analyzed by glancing-angle x-ray diffraction analysis (Read camera) using Cu$K\alpha$ radiation to identify the phases formed. Superconducting transition temperatures (T_c) were measured by the inductive method. The composition of the as-deposited film was analyzed by electron-microprobe analysis and/or MeV Rutherford backscattering analysis. The compositions determined by these two different methods were in agreement within 1 at.%.

III. RESULTS AND DISCUSSION

A. Nb-Al

1. High temperature anneal

Figure 1(a) shows the typical x-ray diffraction pattern

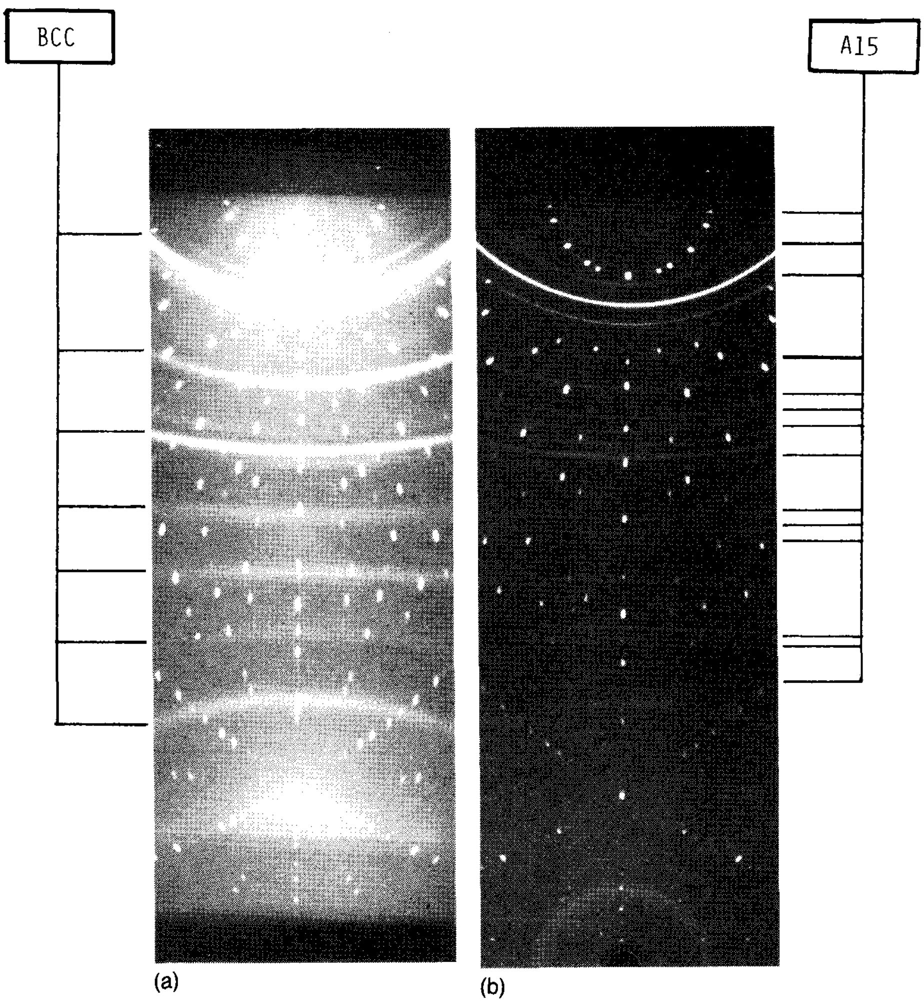

FIG. 1. Read-Camera diffraction pattern for a Nb-Al sample (24.6 at.% Al) (a) as deposited and (b) after laser anneal, 10 scans at 1400 °C.

obtained from as-deposited samples of Nb-Al. The principal lines shown were identified as arising from the bcc structure. Some weak lines from the A15 phase were also observed. A variety of laser-annealing experiments were performed with calculated laser-annealing temperatures (T_{max}) in the range 1300–1800 °C. Figure 1(b) shows the x-ray diffraction pattern of a sample (of 24.6 at.% Al) which was laser annealed at 1400 °C with 10 laser scan frames. Scan lines were overlapped by ~30% in each frame. Formation of the A15 structure after laser annealing is clearly observed, with some weak diffraction lines from the bcc phase. All laser-annealed Nb_3Al samples examined exhibited similar diffraction patterns, where both the A15 and bcc phases exist. The relative abundance of the A15 to the bcc phase varied substantially with the composition of the film and laser-annealing conditions (T_{max} and number of laser scan frames). One important point is that we do not observe any diffraction lines from the tetragonal Nb_2Al phase, which is the second phase typically obtained at lower temperatures. This is particularly important since the phase boundary between the A15 and Nb_2Al phase is at less than 22 at.% Al for temperatures below about 1500 °C.[1–4] This result therefore shows that the cw-laser processing succeeded in quenching the high-temperature phase to room temperature without decomposition into lower-temperature phases that accompanies the conventional thermal-quench method.

In Fig. 2, T_c is plotted as a function of the number of laser scan frames. The laser-annealing temperature is about 1400 °C for all samples. Data are shown for two sets of Nb-Al samples with different compositions (21.0 and 24.6 at.% Al). T_c is found to increase linearly with the number of scan frames up to 10 frames, after which T_c stays nearly constant. X-ray diffraction analysis showed that this T_c enhancement was correlated with the growth of A15 phase relative to the bcc phase. Therefore, 10 laser scans are probably sufficient to carry the reaction to completion. It is also shown in Fig. 2 that T_c is consistently higher for larger Al composition.

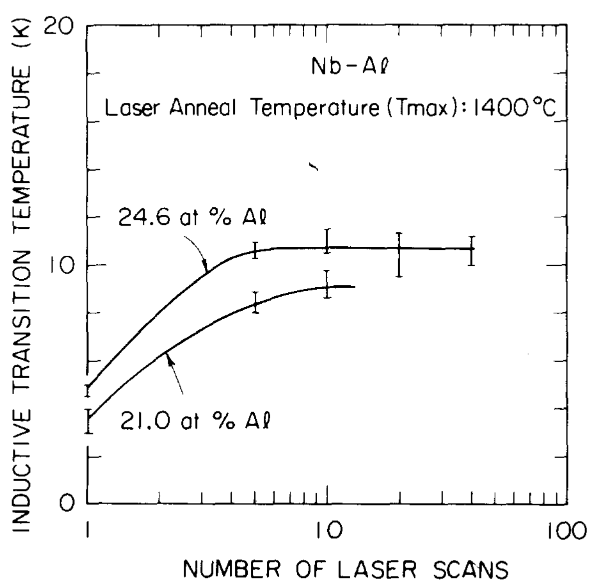

FIG. 2. Superconducting transition temperatures T_c as a function of high-temperature laser scans at 1400 °C for two sets of Nb-Al samples (of 21.0 and 24.6 at.% Al).

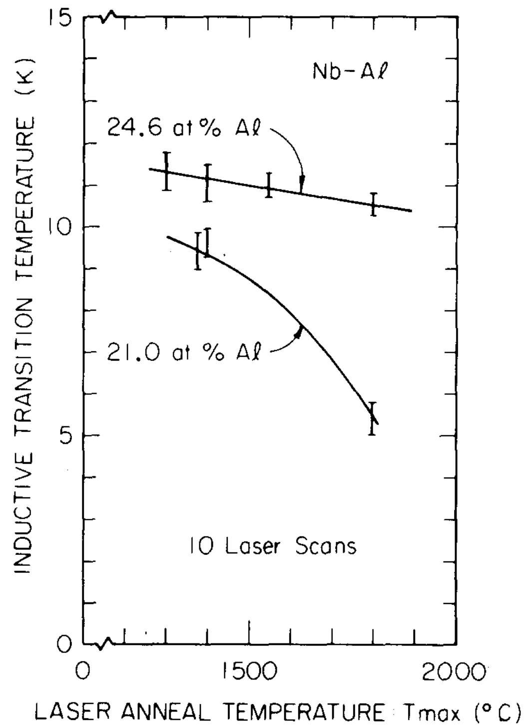

FIG. 3. Superconducting transition temperatures T_c as a function of laser annealing temperature for the same two sets of Nb-Al samples.

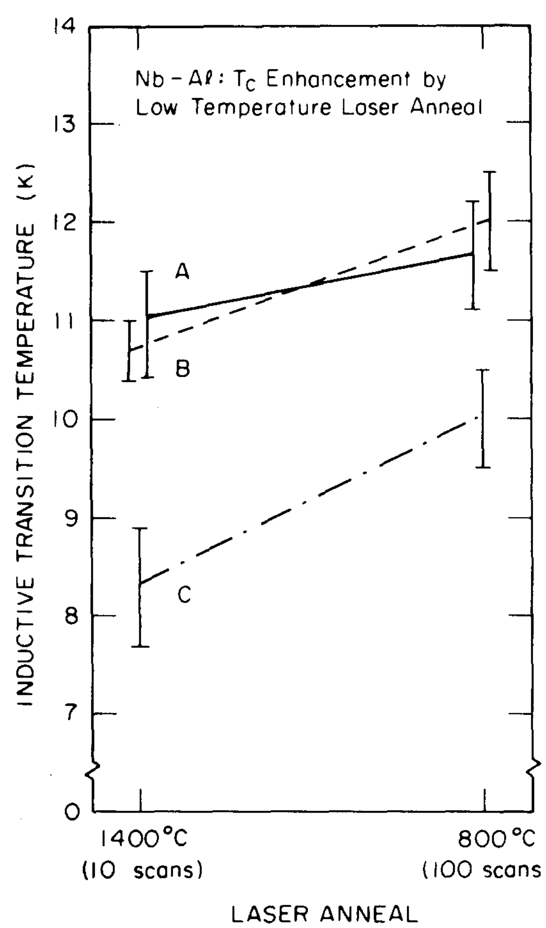

FIG. 4. Superconducting transition temperature T_c as a function of low-temperature laser scans at 800 °C.

TABLE I. Summary of crystalline structures of NbSi films produced by laser annealing.

Laser output power (W)	Composition of NbSi film		
	19.9 at.% Si	20.5 at.% Si	22.8 at.% Si
9	A15 (single phase)	Ti_3P type >> A15	Tetragonal (Cr_5Si_3 type) + Ti_3P type (No A15)
11	Ti_3P type + tetragonal (Cr_5B_3 type)	...	...

Figure 3 shows the dependence of T_c on laser-annealing temperature for the same two sets of NbAl samples as above. Ten laser scans were employed at each temperature. It is seen that higher annealing temperature reduces T_c, particularly for the low-Al-composition (21.0 at.% Al) samples. X-ray diffraction analysis showed that the samples annealed at high temperatures had less A15 phase (and more bcc phase) than the samples annealed at lower temperatures for both Al compositions. These observations are qualitatively consistent with the equilibrium phase diagrams of Nb-Al,[2–4] considering the uncertainty in temperature determinations. Briefly, the compositional range of the bcc solid solution is more Al-rich ($\geqslant 21$ at.% Al) at high temperatures ($\geqslant 1800$ °C). Hence, the increased formation of the bcc phase at high temperatures, particularly for the sample of 21.0 at.% Al, leads to the lower values of T_c.

2. Low-temperature anneal

From the discussion above one can conclude that the high-temperature state in the phase diagram can be quenched to room temperature by scanning cw laser annealing without a corresponding phase change. However, atomic disorder is usually observed following a rapid quench to room temperature. Low-temperature furnace annealing at

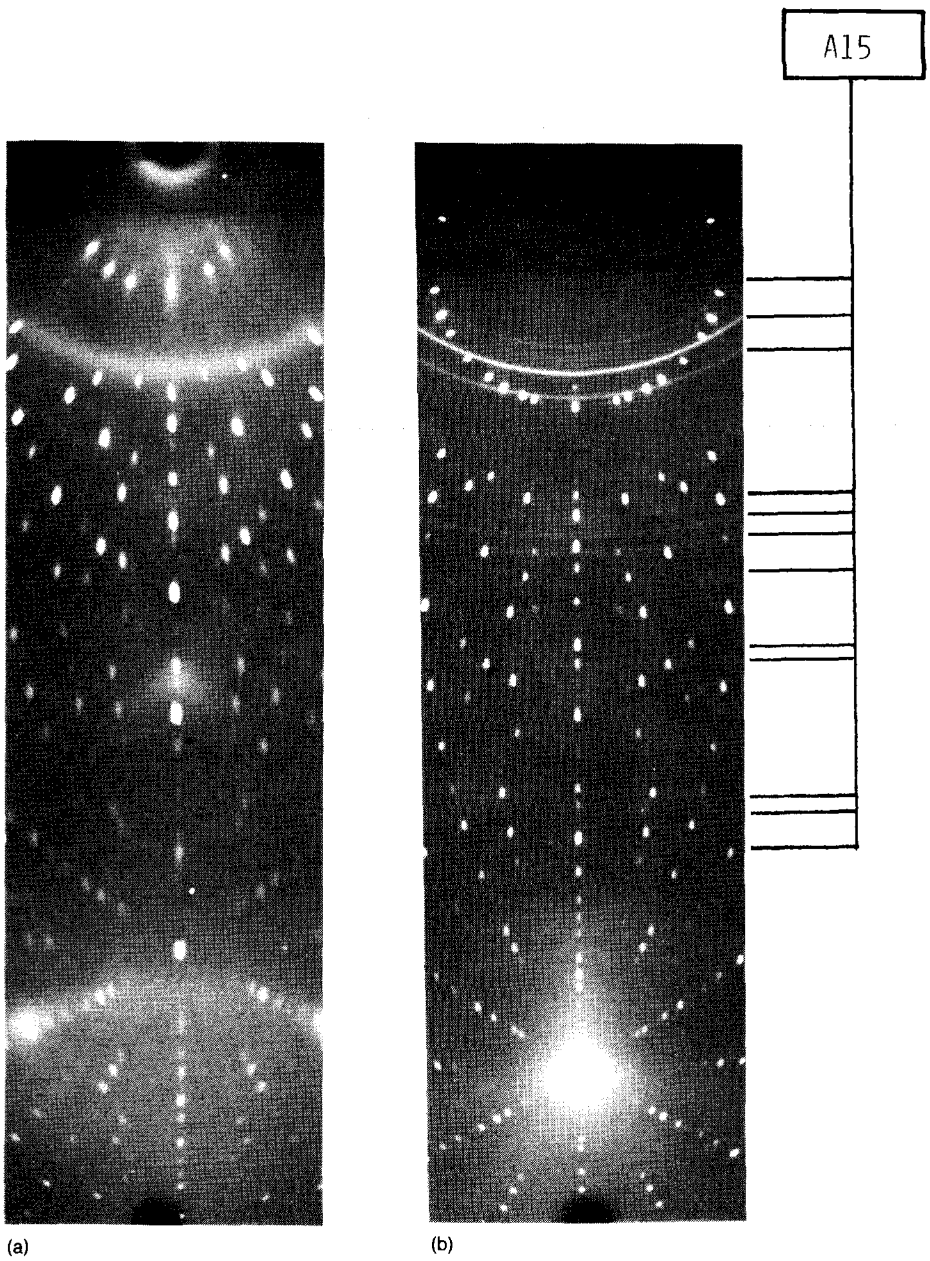

FIG. 5. Read-Camera diffraction pattern for a Nb-Si sample (19.9 at.% Si) (a) as deposited and (b) after laser anneal, 9 W, 1 scan.

700–800 °C can, of course, improve the ordering, but such annealing usually leads to decomposition of the as-quenched phase into the unwanted low-temperature phases.

As discussed earlier, a single laser beam scan is equivalent to furnace annealing for very short times ($\sim$ msec) with very short heating and cooling cycles. By repeated scanning, one can therefore extend the effective annealing time without changing cooling and heating rates. This is exactly what is required for annealing Nb-Al samples. Using such a procedure, three different samples were subjected to 800 °C laser annealing for 100 scan frames. Values of T_c before and after this process are shown in Fig. 4. A T_c enhancement of 0.5–1.5 K is observed for all samples. There is no significant change in the relative amounts of the A15 to the bcc phase, and the second-phase Nb_2Al was not observed in any of these cases. We tentatively attribute this T_c enhancement to the atomic ordering obtained by low-temperature laser annealing.

B. Nb-Si

X-ray diffraction analysis showed that the as-deposited films of Nb-Si (1000 Å) were highly disordered or amorphous. Laser annealing was performed with a scan speed of $\sim$50 cm/sec. The crystal sructures obtained after a single laser scan are summarized in Table I.

Figure 5 shows the x-ray diffraction pattern obtained from the 19.9 at.% Si sample after laser annealing at 9 W. Formation of the single-phase A15 compound is clearly observed. T_c measurements performed on this sample, both resistively and inductively, gave values of $\sim$ 4 K.

From Table I it is seen that the Ti_3P structure was obtained at higher laser annealing temperatures (11 W). Table I also shows that the A15 structure becomes more difficult to form when the composition is close to stoichiometric Nb_3Si.

It should be noted that laser annealing can crystallize 19.9 at.% Si Nb-Si samples to the single-phase A15 structure without melting, while melting is clearly involved in the splat cooling method. This is important because it may permit use of the 19.9 at.% Si compound as a seed layer for subsequent epitaxial growth of a stoichiometric A15 phase. An amorphous Nb-Si film consisting of layers in which the composition changes gradually from 19.9 to 25 at.% would be interesting for laser annealing, since a single laser scan could possibly crystallize the 19.9 at.% Si layer into the A15 phase, which might then propagate to the layer of 25 at.% Si.

IV. CONCLUSIONS

The application of cw laser annealing for the synthesis of superconducting Nb_3Al and Nb_3Si A15 compounds has been demonstrated. For the Nb_3Al system two important aspects of the cw laser process have been shown, viz., the possibility of quenching the high-temperature phase to room temperature without decomposition into low-temperature phases and the use of low-temperature multiple laser scanning for atomic ordering. A T_c enhancement of 0.5–1.5 K is obtained by using 100 laser scan frames at 800 °C without any significant change in the crystal structure of the sample. For the Nb_3Si system we have shown that laser annealing can form a single-phase A15 structure from the amorphous continent without melting. These results suggest that cw-beam annealing offers a very promising approach to synthesize the stoichiometric A15 compounds.

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